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POLYMER MATRIX COMPOSITES**

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SUMMARY

Research at the NASA Lewis Research Center directed toward the application of fiber composites to aeronautical and space vehicle systems indicates the following: It appears quite probable that resin/fiber composites can be developed for service at 315° C (600° F) for several thousand hours and at 370° C (700° F) for a few hundred hours. The retention of resin/fiber strength at these high temperatures can be achieved by modifying the polymer molecular structure or by developing new processing techniques, or both. Carbon monofilament with attractive strength values has been produced and fabrication studies to reinforce aluminum with such monofilaments have been initiated. Refractory wire-superalloy composites have demonstrated sufficiently high strength and impact values to suggest that they have potential for application to turbine blades at temperatures to 1200° C (2200° F) and above. Application of composite materials to hardware requires the development of structural analysis methods to assist in selecting the proper fiber-matrix combination, optimize the laminate configuration and predict failure. Significant progress has been made in developing and applying such structural analysis techniques.

INTRODUCTION

Fiber-reinforced composites and design analysis methods for these materials are being developed at the NASA Lewis Research Center because of the vast potential of composites for decreasing weight and/or increasing use temperature capability in aerospace systems. These composites have potential for use in airbreathing engine components as well as aeronautical and space vehicle structures. Refractory wire-superalloy composites for use up to 1200° C (2200° F) or more and metal-matrix composites for lower temperature applications such as aerospace structures and turbojet fan and compressor blades are under investigation and are discussed.

The development of a number of resin systems, including the polyimides and polyphenylquinoxalines, is described and their potential for use at temperatures approaching 315° C (600° F) is indicated. Various molecular modifications that improve processability and/or increase thermal and oxidative resistance of the resins are also described.

Finally, structural analysis methods are discussed for determining the stresses and deformations in complex composite systems. Consideration is also given to residual stresses resulting from the curing process and to the foreign object damage problem in fan blade applications.

POLYMER MATRIX COMPOSITES

At temperatures up to 260° C (500° F) most thermoplastic and thermoset organic polymers undergo reversible or irreversible changes and exhibit a general loss of mechanical properties. In recent years, numerous polymers have been synthesized which have potential use temperatures of 315° C (600° F) or above (ref. 1). The most noteworthy of the high temperature polymers synthesized to date are the polyimides and the polyphenylquinoxalines. In addition to being noted for their thermooxidative stability, high temperature polymers are difficult to process into useful articles.

The key to synthesizing high temperature polymers is to incorporate aromatic, heteroaromatic and heterocyclic structural units in the polymer molecular structure. These ring structures are able to absorb thermal energy and contain a minimum number of oxidizable hydrogen atoms. Polymers having a multiplicity of stable structural units result from the use of monomers containing aromatic, heteroaromatic and heterocyclic rings and from polymerization reactions forming such ring structures. The inherent stiffness of the thermooxidatively stable ring structures and the condensation polymerization reactions leading to their formation are responsible for the inferior processing characteristics of high temperature polymers. The infusible nature of ring stiffened polymer molecular structures prevents or limits polymer flow and consolidation. Volatilization and entrapment of the condensation reaction byproducts leads to the formation of voids in the finished article. The presence of these voids seriously degrades both the mechanical properties and the long term thermooxidative stability.

Addition-Type Polyimide Composites

One of the recent breakthroughs in high temperature polymer chemistry was the NASA sponsored development of a novel class of polyimides which cure by an addition reaction (ref. 2). The approach uses low molecular weight amide-acid prepolymers end-capped with reactive alicyclic rings that polymerize into thermooxidatively stable cross-linked polyimides without the evolution of by-products. The molecular structure of a commercially available A-type amide-acid prepolymer known as PL3N is shown in Fig. 1(a). The prepolymer has a formulated molecular weight of 1300 and is supplied as a 40 percent by weight solids solution in dimethylformamide. Following impregnation of the reinforcing fibers with the prepolymer solution the prepreg is heated at temperatures up to 205° C (400° F) to cause imide ring formation and solvent removal (fig. 1(b)). Final polymerization occurs at elevated temperatures and pressures through the end groups.

Thermooxidative Stability. - Fiber reinforced PL3N A-type polyimides are able to retain useful properties at 315° C (600° F) in air for about 100 hours. An A-type polyimide known as P10P having improved thermooxidative stability at 315° C (600° F) was developed in the work reported in Ref. 3. Prepolymer

PIOP differs from PI3N in the following two respects: (1) PIOP has a formulated molecular weight of 1000 compared to 1300 for PI3N, and (2) the dianhydride used in PIOP is pyromellitic dianhydride (PMDA) rather than 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA). The weight loss of unreinforced, completely cured PIOP after 300 hours exposure in air at 315° C (600° F) was 4.5 percent compared to 10.5 percent for PI3N tested under identical conditions.

A major short coming of A-type amide-acid prepolymer solutions, particularly PIOP prepolymer solutions, is that they exhibit variable shelf-life characteristics. In our composites studies with PIOP we have observed the presence of gel and/or precipitate in solutions containing 40 percent solids within two days of prepolymer synthesis. Of course, this gelation/precipitation phenomenon can be minimized by diluting the solution to lower the solids content. Another method to assess solution stability is to monitor the variation of solution viscosity with time. As it can be seen in the upper curve of Fig. 2, the solution viscosity of a 20 percent solids PIOP solution markedly decreased during the first two hundred hours. This viscosity decrease can be attributed to cleavage of the amide carbon-nitrogen bond resulting in prepolymers of lower molecular weight. The variable shelf-life characteristics of addition-type amide-acid prepolymer solutions detracts from their usefulness as impregnating solutions. Another shortcoming of the addition-type amide-acid prepolymer approach is that toxic, high boiling solvents such as dimethylformamide (DMF) are required. At the temperatures required to effect solvent removal it is possible for the solvent to form relatively stable complexes with the prepolymer. These complexes can either prevent imide ring formation, lowering the thermooxidative stability or volatilize during the final cure forming voids in the end-use item.

Studies performed at the NASA Lewis Research Center by one of the authors and his co-workers (ref. 4) have demonstrated a new approach to synthesize processable addition-type polyimides. In this approach a mixture of appropriately modified anhydride and dianhydride monomers together with an aromatic diamine was placed into solution rather than synthesizing end-capped amide-acid prepolymers. The structures of the modified anhydride and dianhydride reactants are shown in Fig. 3. It can be seen in Fig. 3 that the modification consists of forming the monomethyl and dimethyl esters of the respective dicarboxylic and tetracarboxylic acids. Because these esters have limited reactivity at room temperature with amines, stable solutions of the esters and aromatic diamines can be formed. The variation of solution viscosity for what we call monomeric reactant solutions is shown by the lower curve of Fig. 2. In contrast to the behavior of the end-capped amide-acid prepolymer solution (upper curve of fig. 2) the viscosity of the monomeric solution shows a small increase. The increase in solution viscosity can be attributed to the formation of low molecular weight oligomers which do not appreciably alter viscosity and shelf-life. For comparison purposes the data reported in Fig. 2 for the monomeric reactant and prepolymer solutions were for 20 percent solids in DMF. However, it is not necessary to use DMF as the solvent for the monomeric mixture. Methanol is the solvent routinely employed in our studies (ref. 5). Methanol solutions with solids contents in the range of 60 to 70 percent can be easily formed and used for impregnating advanced fibers such as graphite.

Several important processing considerations for addition-type monomeric reactant and prepolymer, and condensation-type polyimide resin are summarized in table I. As may be seen from table I, the monomeric reactant approach avoids the problems encountered with condensation-type and prepolymer addition-type polyimides. Two additional advantages of the monomeric reactants approach are that: (1) monomeric reactant solutions can be prepared, as needed, by relatively unskilled personnel--compared to the current practice of using highly trained polymer chemists to conduct prepolymer synthesis and, (2) materials handling logistics are greatly simplified--only the monomer powders need to be shipped and/or stored.

The increased thermooxidative stability of PIOP compared to PI3N can be attributed to the use of PMDA instead of BTDA as the dianhydride moiety. Another approach to increase the thermooxidative stability of addition-type polyimides is to decrease the alicyclic content of the cured polymer. A-type prepolymers containing PMDA and having formulated molecular weights (FMW) greater than 1000 were reported to possess inadequate resin flow and had lower thermooxidative stability (ref. 3). Moreover, solutions of higher FMW A-type prepolymers are viscous and have the stability problems previously described. The monomeric reactants approach affords a convenient method of investigating the effect of varying the chemical composition and/or stoichiometry of monomeric reactant solutions on composite thermooxidative stability. The results of a preliminary investigation using monomeric reactant solutions differing in chemical composition and/or stoichiometry are summarized in table II. The data have been taken from Ref. 4. Samples A and B; and C and D were formulated to have the chemical composition of PIOP and PI3N, respectively. Their stoichiometries were adjusted to approximate prepolymers having formulated molecular weights of A = 1000, B = 1750, C = 1500 and D = 3000. The 600-hour, 315° C (600° F) composite weight loss data for samples A and B (18 percent) compare favorably with the 500-hour, 315° C (600° F) weight loss (14 percent) for PIOP-T50S graphite fiber composites (ref. 3). The composite weight loss data of sample C was lower than anticipated. The superior thermooxidative stability of the polyimide composite made with BTDA as the dianhydride moiety, compared to that made with the PMDA moiety (weight loss sample C less than weight loss sample A) appears to be contradictory to the findings of Ref. 3 which were previously discussed. Apparently in the studies reported in Ref. 3, the greater thermooxidative stability of PMDA compared to BTDA overshadowed the higher alicyclic content of PIOP (30 percent higher than for PI3N). However, for sample C the further reduction of alicyclic content (13 percent lower alicyclic content than for PI3N) enhanced the thermooxidative stability to a greater extent than did the inclusion of PMDA in PIOP. A comprehensive investigation was conducted at NASA Lewis (ref. 5) which in part was directed toward establishing the validity of the above finding. The composite weight loss characteristics of monomeric reactant polyimides (chemically similar to PI3N but having lower alicyclic contents) HTS graphite fiber composites at 315° C (600° F) as a function of exposure time in air were reported in Ref. 5 and are shown in Fig. 4 of this report. The formulated molecular weights of samples 1 to 3 are 1500, 1750, and 1900, respectively. Sample 6 is chemically and stoichiometrically similar to PIOP and was included for comparative purposes. It can be seen in Fig. 4 that the composite weight loss for samples 1 to 3 was considerably lower than that of sample 6. Because of the vagaries of isothermal analysis, it is difficult to attach too much significance to the weight loss differences, among samples 1 to 3. However, it is significant to note that the average composite weight loss for samples 1 to 3 after 600 hours was 39 percent lower than the weight loss for sample 6. These results clearly substantiate the finding that reducing the alicyclic content of A-type polyimides containing BTDA as the dianhydride moiety can result

in a significant improvement in thermooxidative stability.

Interlaminar shear strength. - Figure 5 shows the variation of interlaminar shear strength for samples 1 to 3, and 6 after exposure at 315° C (600° F) as a function of exposure time. Also presented are the room temperature and short time 315° C (600° F) properties. The room temperature values are somewhat higher than those previously reported for A-type polyimide/HTS graphite fiber composites (ref. 6). The large difference between the room temperature and short time 315° C (600° F) values of interlaminar shear strength appears to be a phenomenon associated with intermediate modulus graphite fibers derived from polyacrylonitrile (PAN) fibers.

Because the interlaminar shear strength of samples 1 to 3 increased during exposure at 315° C (600° F), it appears that these samples underwent a postcure, whereas the interlaminar shear strength decrease for sample 6 can be attributed to oxidative degradation. The important fact to note is that the interlaminar shear strength of samples 1 to 3 remained nearly constant from 100 to 600 hours. After 600 hours of exposure at 315° C (600° F) the average interlaminar shear strength of samples 1 to 3 was approximately 35 percent higher than that of sample 6. To the authors' knowledge the data for samples 1 to 3 represent the best interlaminar shear strength retention for A-type or C-type polyimide graphite fiber composites reported to date. The interlaminar shear strengths of samples 2 and 3 began to decrease after reaching maximum values after 200 hours of exposure. These results are somewhat contrary to the expected improvement in thermooxidative stability that should have resulted for samples 2 and 3 which have lower alicyclic contents than sample 1. It should be pointed out that the composite weight loss data (fig. 4) and interlaminar shear strength data (fig. 5) were obtained from laminates fabricated according to a procedure which had been optimized for A-type amide-acid prepolymer solutions rather than monomeric reactant solutions. Further work is currently in progress to determine if the interlaminar shear strength retention characteristics of samples 2 and 3 can be improved by optimizing the fabrication process for monomeric reactant solutions.

It is entirely possible that optimization of the fabrication process will enable addition-type polyimides to be used which have formulated molecular weights in the range of 4000 to 6000. The thermooxidative stability of these addition-type polyimides should make it possible to extend the use time for A-type polyimide graphite fiber composites at 315° C (600° F) to several thousand hours.

Polyphenylquinoxalines for composites. - Another class of high temperature polymers which have the potential of extending the continuous use temperature-time limits of resin/fiber composites are the polyphenylquinoxalines (PPQ's). Polyquinoxalines were synthesized by workers in France and the United States at about the same time (refs. 7 and 8). Polyquinoxalines cannot withstand continuous exposure for times greater than 400 hours in air at temperatures of 315° C (600° F) and above. The pyrazine hydrogen atom of the quinoxaline ring is thought to be the reaction site for thermooxidative degradation. In an attempt to improve the thermooxidative stability of polyquinoxalines, modified polyquinoxalines in which a phenyl group was substituted for the pyrazine hydrogen atom were synthesized (ref. 9).

NASA Lewis Research Center is sponsoring research (ref. 10) to develop PPQ's for use as matrix materials in high temperature resin/fiber composites. A number of different PPQ's based on the repeat units shown in Fig. 6 have been synthesized. The 315° C (600° F) weight loss characteristics of a low molecular weight (LMW) PPQ-I, an intermediate molecular weight (IMW) PPQ-II, and random and block PPQ copolymers for various polymer film thicknesses are summarized in table III. The low and intermediate molecular weight versions of PPQ-I and PPQ-II correspond to inherent viscosities (η_{inh} , 0.5%, H_2SO_4 at 25° C) of less than 1.0 and 1.0 to 2.0 dl/g, respectively. The stoichiometric ratios of monomers I, II, and III were 1.0:0.25:0.75. The initial weight loss which occurred during the first 25 hours can be attributed to the loss of residual solvent (m-cresol) and unreacted monomers. It can be seen from the data of table III that the PPQ's based on monomers I, II and III are quite resistive to thermooxidative degradation at 315° C (600° F). It appears that these PPQ's have excellent potential for extending the use temperature-time performance limits of polymer matrix composites to 370° C (700° F) for a few hundred hours.

METAL MATRIX COMPOSITES

One of the advantages of fiber reinforced composites is that the component materials can be selected to meet specific service requirements. Polymer matrix composites are superior for some applications and metal matrix composites for others. Metals are generally preferred where a tougher, more temperature resistant matrix is required. However, the higher temperatures generally required for fabrication are disadvantageous. Fiber-matrix reactions are one of the problems associated with the higher fabrication temperatures and steps must be taken to minimize the property loss that could otherwise result. Some steps that can be considered are: coating of fibers to form a diffusion barrier, selection of relatively compatible fiber-matrix combinations and modification of processing variables to reduce diffusion rates. Fiber diameter is another variable that might be used to facilitate composite fabrication, reduce the extent of reaction and improve composite properties. Such is the case for carbon filaments used for metal matrix composites.

Carbon-Aluminum Composite Development

Carbon filaments obtained by pyrolysis of organic fibers have excellent properties which are used effectively in polymer matrix composites. Unfortunately, these small diameter, 6-8 micrometer, fibers are not well suited for metal matrix composites because of fiber-matrix reaction and fabrication problems. A larger diameter monofilament would be advantageous because it could more easily be coated with a diffusion barrier and the smaller number of fibers for a given volume fraction fiber content would make fabrication of a composite specimen easier.

Since large diameter monofilaments were not available, NASA Lewis Research Center has undertaken a contract program to develop methods to produce them. One of the methods studied was, chemical vapor deposition on a heated carbon substrate. Process conditions were evolved which enabled the production of

monofilaments on 33 micrometer (1.3 mil) diameter carbon substrate using various ratios of borane and ethylene gases. The tensile properties of large diameter carbon base monofilaments produced by the CVD process technique developed (refs. 11 and 12) compare favorably with the properties of other filaments. Figure 7 shows the density normalized strength of 80 micrometer (3.5 mil) diameter carbon monofilament relative to boron monofilament and small diameter, 6-8 micrometer, carbon multifiber yarn. The data of Fig. 7 were obtained at room temperature, but the relative values shown would be expected to apply at temperatures to 480° C (900° F). Increased strength of the CVD carbon monofilament compared with those indicated in Fig. 7 is expected with improved understanding and control of production variables.

While improvements in monofilament production are anticipated the current material is satisfactory for initial composite studies. Over 40,000 meters (130,000 ft) of the CVD monofilament has been produced and initial composite fabrication process development for carbon-aluminum composites has begun. It is expected that process techniques similar to those developed for the production of boron-aluminum composites can be adapted to the production of carbon monofilament-aluminum. Aluminum matrix carbon composites offer the potential for a lower density composite than boron-aluminum which may be applied to fan and compressor blades as well as other structural components.

Tungsten Wire-Superalloy Composite Development

Metal matrix composites also offer the potential for application to high temperature components such as advanced aircraft engine turbine blades. Refractory metal wire-superalloy composites which have been investigated at a number of laboratories (refs. 13-17) have the potential of combining the high temperature strength of a refractory metal with the oxidation resistance, toughness and ductility of a superalloy. Several problems must be overcome, however, to achieve the desired combination of properties. Inter-diffusion and reaction at the fiber-matrix interface can degrade fiber properties and thereby the composite properties. Also, tungsten, one of the principal refractory metals considered as a reinforcement fiber, loses much of its ductility below the ductile brittle transition temperature (150-370° C, 300-700° F for tungsten wire). For aerospace use, the high density of most refractory metal alloys must also be accommodated. These problems have been recognized and progress has been made in overcoming them. The current status of development of refractory wire-superalloy composites will be reviewed in the following portion of this paper with a particular view toward their potential for application to turbine blades for advanced aircraft gas turbine engines.

Refractory wire development. - The need for refractory alloy fibers with improved strength was recognized early in the superalloy composite program at the Lewis Research Center and a continuing effort to fabricate and evaluate stronger alloy wire was initiated as part of the composite program. Alloys of molybdenum, tantalum, columbium, and tungsten have been fabricated into wire for use in composites as part of this program (refs. 18-22). The wire properties shown in Fig. 8 indicate the stress/density values for 100 hour rupture life at 1090° C (2000° F) for some of the wires developed as part of that effort. The data for 218 alloy lamp filament wire and for conventional bulk superalloys are included for comparison. The high strength achieved for the wires developed is readily apparent with about a three fold stress/density advantage for the W-Re-Hf-C alloy wire (W-4.1Re-0.38Hf-0.021C) over the 218 wire. The difference in stress/density between the W-Hf-C wire (W-0.33Hf-0.042C) and the W-Re-Hf-C wire is at least in part due to thermomechanical fabrication differences and off-optimum composition. The B-88 columbium alloy wire is superior to the 218 wire at 1090° C (2000° F) and is primarily intended for use at temperatures below 1090° C (2000° F) where it has a potential advantage. The very high strength of these wires indicates a potential for achieving high composite properties where the fiber strengths can be realized within the superalloy matrix. Additional improvement in wire fabrication processing can be expected which should further increase strength and productivity at reduced cost. The refractory metal alloys which were included in the wire development program had been developed for rod or sheet applications at higher use temperatures than currently proposed for refractory wire-superalloy composites. The rupture properties of the wires in most cases were superior to those for sheet, rod, or foil at the composite use temperatures. It is believed, however, that there is considerable opportunity for further refractory alloy composition development, which coupled with improved thermomechanical fabrication processing can produce wire with strength optimized for use in superalloy composites.

Composite rupture strength. - Composites with excellent rupture strength can be achieved if wire properties such as those in Fig. 8 can be realized within the superalloy matrix. However, except for a few systems, metal fibers react with metal matrices thereby causing varying degrees of property loss. Interdiffusion, reaction and recrystallization can reduce wire strength and ductility. Therefore, control of matrix-fiber interaction is necessary during composite fabrication and throughout the service lifetime. Diffusion barrier coatings on the wire are a potentially effective way to achieve such control. Unfortunately techniques attempted in the past have not resulted in reproducible and successful barrier coatings for refractory alloy wires. Since diffusion barriers are not presently available alternate methods have been used to control reactions. Thus, specific fabrication processing variables have been selected to minimize the extent of interaction for most refractory wire-superalloy composite systems. Many investigators (refs. 15, 23-25) have used solid state processing, either powder metallurgy, or foil-wire compaction. Other investigators have used liquid phase or casting techniques (refs. 14, 16 and 26) and some attempts have been made to limit fiber-matrix reaction.

The refractory wire-superalloy composite program at the Lewis Research Center used a combination of factors, including fabrication processing, matrix alloy composition, and fiber diameter to control matrix fiber reaction (refs. 27 and 28). The fabrication process was developed to limit reaction during composite fabrication while matrix composition and fiber diameter were selected to control service exposure reaction. A slip casting-hot pressing process was used to take advantage of the lower diffusion rates of solid state sintering rather than the more damaging liquid phase methods. Furnace sintering was conducted in a hydrogen atmosphere at a relatively low temperature, 815° C (1500° F) to remove surface impurities on the powder and to partially densify the body. Removal of impurities was intended to reduce the extent of reaction from rapidly diffusing surface contaminants. Two stage hot pressing was used to obtain as dense a body as possible before exposing the composite to high temperature because the higher density body would have lower diffusion rates than a porous body. Matrix alloy compositions were selected to reduce the tendency for solute diffusion into the fiber. These alloys contained high weight percentages of refractory metals

to reduce diffusion penetration kinetics and recrystallization. Titanium and aluminum additions to the matrix were made to form intermetallic compounds which could further reduce the diffusion of nickel and increase matrix strength. The final step taken to maximize retained composite strength was to select wire diameter to increase the size of the unreacted wire core. The depth of penetration of reaction is essentially the same for a 0.20 mm (8 mil) diameter fiber as for a 0.50 mm (20 mil) diameter. By using larger diameter wire the percentage of unreacted fiber core was increased. However, smaller diameter wires are usually stronger so a balance must be achieved between the two effects. The larger diameter wire 0.38-0.50 mm (15-20 mil) was superior for service times of 100 hours or more (ref. 27).

Composite specimens have been fabricated using the techniques described and data for several refractory wire-superalloy composites are shown in Fig. 9. Data for conventional superalloys and directionally solidified eutectic composites are also included for comparison. The data are normalized for density variation to permit cross-comparison. The nickel base alloy (Ni-25W-16Cr-2Al-2Ti) developed to reduce matrix-fiber reaction was used as the matrix for all three refractory wire composites. The data for 218 wire composites and W-2ThO₂ wire composites (refs. 27 and 28), compare favorably with those for superalloys and eutectics.

The W-Hf-C wire composites contained wire recently produced as part of our continuing wire development program. The W-Hf-C composite has about 2540 m (100,000 in.) or over four times the strength/density value of superalloys and over twice those of the best published values for directionally solidified eutectics. This advantage in specific strength may be used to increase service life or operating temperature or both. This comparison was based on data obtained from composites containing wires without diffusion barriers. As such, composite data were influenced by matrix-fiber reaction. Matrix element diffusion into the wire caused about 30 percent reduction in wire stress rupture strength compared to that without matrix-fiber reaction. The reduction was attributed (ref. 27) to diffusion triggered recrystallization of an outer layer of the wire. Based on limited metallographic data (ref. 29) diffusion barrier coatings are expected virtually to eliminate such losses. A problem to be overcome is the development of methods to reproducibly and uniformly apply well bonded barriers. The author is optimistic that barrier coatings will be achieved soon and this will serve to increase both strength and use temperature.

Figure 10 illustrates a projection of the properties that might be achieved with diffusion barrier coated refractory alloy wire composites and directionally solidified eutectics. The property plotted is density normalized 1000 hour rupture strength at 1090° C (2000° F). The refractory wire-superalloy composite strengths shown are from four to six times those for the eutectics. The composite data were calculated using wire data from Fig. 8 assuming negligible matrix strength contribution and a 5 percent loss in wire strength from fiber-matrix reaction. Such a reactivity loss could result from localized breakdown of the diffusion barrier. It is evident from the comparisons in Figs. 9 and 10 that refractory wire-superalloy composites have excellent rupture strength and that there is potential for further increases. These comparisons also suggest that such composites have excellent potential for use in turbine blades at operating temperatures higher than those currently used.

Impact strength. - Materials must display other properties in addition to high rupture strength to be suitable for turbine blade use. One such property is the ability to resist impact failure from foreign objects and fragments from failed components that may pass through the engine. The impact resistance necessary for turbine blades is not clearly related to laboratory impact data. Simulated engine tests with rotating components or actual engine service experience are necessary to fully prove a material for turbine blade application however experimental materials which displayed limited impact strength in pendulum impact tests also have been operated successfully as turbine blades in engine tests. Alloys with miniature Izod pendulum test impact values less than 1.7 joules (15 in. lb) have been successfully run as turbine blades (refs. 30 and 31). Based on this information the value of 1.7 joules was taken as a minimum standard value for miniature Izod impact test data to indicate if a material has promise for further evaluation leading to turbine blade use.

Pendulum impact strength of refractory wire-superalloy composites has been measured (refs. 28 and 32). Miniature Izod data obtained for composites over a range of temperatures are shown in Fig. 11(a). Charpy impact test data obtained for composites at 1090° C (2000° F) and for conventional superalloys at 870° C (1600° F) are shown in Fig. 11(b). The composites were slipcast and hot pressed using 218 lamp filament wire and a matrix of the nickel alloy designed for compatibility (ref. 27). The miniature Izod impact strength values of the composite above the ductile-brittle-transition temperature (DBTT) of the tungsten wire, which is about 260° C (500° F), were well above the minimum standard for turbine blades. The Charpy test values for the composite at 1090° C (2000° F) were well above those for the conventional superalloys at their normal operating temperature in turbines. Thus, the composite impact values can be considered acceptable for turbine blade use above the DBTT of the tungsten wire where plastic deformation of the wire can contribute significantly to the composite impact strength. At temperatures below the DBTT of the wire however the miniature Izod data for the as-hot-pressed composite was below the minimum standard. However, as shown in Fig. 12, the composite impact strength can be improved to meet or exceed turbine blade requirements. The room temperature data of Fig. 12 show that the impact strength of the as-hot pressed composite is below the minimum standard. Heat treatment for 100-250 hours at 1090° C (2000° F) or hot rolling the composite increased the room temperature impact strength to values well above the minimum standard.

The improved impact strength was related (ref. 32) to improved matrix impact strength. Scanning electron micrographs of fracture surfaces showed increased bonding of matrix powder particles and evidence of plastic deformation of the matrix after rolling or heat treatment. Similar fracture micrographs of as-hot-pressed composite specimens showed much less bonding and very little matrix deformation. Secondary deformation of powder metallurgy matrix composites can readily be accomplished by hot forming in closed dies. However it is expected that blade airfoils will be fabricated using diffusion bonding of foil-wire lay-ups. Excellent matrix toughness could be achieved by this method without the need for secondary fabrication.

Oxidation. - Relatively little data have been obtained to determine the relative oxidation resistance of composites and further research is necessary to more fully evaluate them. Most of the data that have been obtained have been sufficiently encouraging to justify additional research. Oxidation data have been

obtained for slow moving furnace air exposure for times to 500 hours at temperatures of 1090° C (2000° F). No visible oxidation of the tungsten wire was found when it was protected by a few tenths of a millimeter of superalloy matrix (ref. 14). Similar results have been obtained (ref. 14) for composite specimens exposed to 1090° C air moving at 1.85 m/sec (6 ft/sec). When tungsten fiber ends were exposed to 1090° C air moving at 1.85 m/sec (6 ft/sec) for 100 hours, only a 2.5 mm (0.1 in.) length of the approximately 1 mm diameter wire was oxidized. This very slight depth of oxidation below the surface of the exposed wire end is encouraging since it suggests that local defects in the protective matrix coating would not cause a large loss of fiber. Such defects in the coating can occur from blade fabrication processing or from foreign object damage during engine service. There remains the task of determining the oxidative behavior of composites when they are exposed to erosive high velocity gas streams and cyclic temperature operation that is typical of aircraft engine service conditions. This represents a more severe requirement than has been evaluated in laboratory tests to date, since temperature cycles can cause spalling of protective oxide films and the erosive scrubbing action of the high velocity gas stream also removes material.

Oxidation protection will be a critical requirement to achieve composite turbine blade operating temperatures above 1090° C (2000° F). Superalloy composition for the airfoil can be selected to provide ductility and erosion and oxidation resistance, particularly where fiber-matrix reaction control is provided by a diffusion barrier. For composites with uncoated wire, the matrix composition can be varied to provide an oxidation resistant outer layer and a more compatible composition near the fibers.

Mechanical and thermal fatigue. - A limited number of high cycle fatigue studies of refractory wire-superalloy composites have been conducted. Additional laboratory data are needed to evaluate the quantitative behavior of the material and to estimate their potential for turbine blade service. High cycle fatigue resistance of Hastelloy X and Nimocast 258 reinforced with tungsten wire was improved relative to unreinforced Hastelloy X and Nimocast 258 (refs. 14 and 33). However, tungsten wire reinforcement did not increase the fatigue strength of Nimocast 713C (ref. 26). The lack of improvement in the fatigue strength in Ref. 26, in contrast to the results of Refs. 14 and 33, was attributed to low resistance to crack propagation in the relatively brittle 713C alloy matrix, and the poor crack stopping ability of the large diameter wires used in Ref. 26. The small number of large diameter, 0.13 cm (50 mil), wires used in Ref. 26 would be expected to be less effective as a crack stopper compared with the smaller diameter, 0.025 cm (10 mil) wires used in Refs. 14 and 33. Increased matrix ductility which might increase resistance to crack initiation also would be advantageous in enhancing fatigue resistance.

Thermally induced low cycle fatigue requirements may be critical for aircraft turbine blade application of composites. Stresses may be generated by the thermal gradient between different portions of the blade during transient temperature operation as well as by the thermal expansion difference between the refractory wire and the superalloy matrix. It will be necessary to use ductile matrix materials which hopefully can relieve such induced stresses by plastic deformation. Some variation in results were obtained for the very few data points published for thermally cycled refractory wire composite specimens (refs. 16 and 26). Matrix cracking has been observed with cylindrical specimens of tungsten wire-cast Inco 713C composites heated in fluidized beds. Similar specimens containing 20 v/o wire (1 or 1.3 mm diam.) showed no cracking after several hundred fluidized bed heating cycles between 550° and 1050° C (1020° and 1920° F) (ref. 26). While matrix cracks were observed after as few as two thermal cycles tensile tests conducted on specimens thermally cycled and cracked showed no strength loss.

Further testing is necessary to indicate the seriousness of this failure mode and to evaluate possible corrective measures. Ability to resist thermal fatigue failure may be critical for aircraft engine service, but may be of little concern for blades used in gas turbine powered electric power generation systems. Continuous or very long time periods of operation are the norm for base load power generating plants. These advanced power systems also require very high turbine inlet temperatures and refractory wire-superalloy composites may be well suited for such service.

Density. - A persistent concern held about tungsten wire-superalloy composites has been that there is a weight penalty associated with their use despite the superior strength/density values of the material compared with superalloys. However, turbine blade weight for a solid blade of tungsten wire-superalloy composite need not exceed that for a similar blade of conventional superalloy if reasonable measures are taken in design and fabrication of composite. Two variables can be used to overcome the high density of the refractory alloy wire. The fiber content can be varied along the blade span so as to tailor strength to that needed, and the blade airfoil thickness near the base can be slightly reduced compared with a superalloy blade because of the improved strength/density properties of the composite.

Fiber content variation, or selective reinforcement, can reduce the average fiber content significantly. Sample blade density calculations made to illustrate the effectiveness of selective reinforcement are shown in table IV. Calculations were made for both uncoated and diffusion barrier coated refractory wire composites. The airfoil matrix alloy for the uncoated wire was the NASA nickel base alloy developed for compatibility with tungsten wires (ref. 27). A 30 percent wire strength loss was assumed to occur from matrix-fiber reaction. This value is about that observed for the composite data obtained thus far in Lewis Research Center studies (refs. 27 and 28). A conventional superalloy IN 100 was selected as the matrix for the diffusion barrier coated wire composite calculations. A 5 percent wire strength loss was assumed for the wire with a diffusion barrier. Blade bases of both composites were assumed to be of IN 100 alloy. Calculations of composite blade fiber content and density were made for a range of blade use temperatures.

The calculation was made for a standard solid blade geometry and the centrifugally induced stresses that would be generated at about midspan in the airfoil of such a blade. Midspan stresses in a typical solid superalloy blade were taken (ref. 13) as a range from 103 to 138 MN/m² (15,000 to 20,000 psi). Since the stresses generated in rotating blades are density dependent, a stress/density value was used. The stress/density value at midspan in a blade made of a typical superalloy with a density of 8.3 gm/cc (0.3 lb/in.³) would range from 1270 to 1695 m (50,000 to 66,700 in.). The stress/density value used for the calculations was taken as 1525 m (60,000 in.), about the middle of that range.

The density values in table IV for varied fiber content fiber composite blades ranged from 8.8 to 10.2 gm/cc (0.32 to 0.37 lb/in.³). High strength superalloys which have about a 980° C (1800° F) use temperature limit as turbine blades have densities as high as 8.97 gm/cc (0.325 lb/in.³), (ref. 16). Thus, the blade density values in table IV for the varied fiber content blades ranged from within the density range for superalloys to about 20 percent above that for superalloys. The relatively low density values for the composite were possible because the average fiber content was 15 volume percent or less. The maximum fiber content at any one cross section of the blade was less than 35 volume percent for all four composite calculations. The low average fiber content means that little reduction in blade airfoil thickness near the base is required to reduce overall blade weight to values equal to those for superalloys.

According to blade designers, reductions in blade thickness or taper, is aerodynamically acceptable and may be advantageous. Blade geometry design is a compromise between aerodynamic and material considerations. Material limitations sometimes lead to blade thicknesses near the airfoil base that result in aerodynamic penalties, and usually result in tapers greater than are aerodynamically necessary. Material with higher stress/density values, such as the refractory wire-superalloy composites, may permit a better compromise in blade geometry design which can produce a blade of equivalent weight and at the same time may permit increased temperature use.

Advanced Aircraft Gas Turbine Blade Application

Figure 13 shows the possible aircraft engine blade use temperature range of refractory wire-superalloy and directionally solidified eutectic composites along with those for superalloys based on the data from Figs. 9 and 10. Rupture strength data for 1000 hour life have been normalized for density. The horizontal band represents a range of stress/density, values that might be required for turbine blades in advanced aircraft gas turbine engines. The blade use temperature range of the refractory wire composite is 1150° to 1260° C (2100° to 2300° F) or about 165° to 280° C (300° to 500° F) above that of superalloys. The eutectic composites had 40° to 80° C (70° to 150° F) higher use temperatures than the superalloys. The lower portion of the refractory wire composite use temperature band can be achieved with uncoated wire reinforced composites while the higher portion will probably require diffusion barrier coated wire.

The increased use temperature which may be possible through the application of solid blades of refractory wire-superalloy composites is significant, however turbine engine designers want to take advantage of the higher efficiencies gained by going to flame temperatures, over 1650° C (3000° F). Turbine blade cooling will be required to operate with any superalloy or superalloy composite blades at these very high flame temperatures. Several blade types have been studied for such cooling. Convection cooled blade designs are simple and more readily fabricated, but require higher cooling air flow rates because of lower cooling efficiency. Film cooled blades are more complex but require less cooling air flow to reach tolerable blade material temperatures. However, as can be seen in Fig. 14 (ref. 34) operation at turbine blade material temperatures of 1150° to 1200° C (2100° to 2200° F) with a convection cooled blade might permit turbine inlet temperatures over 1650° C (3000° F). Further it can be seen, Fig. 14, that cooling flow requirements for such a convection cooled composite blade would be equal to or less than those required for superalloy blades film cooled to 980° C (1800° F), about the operational limit of superalloys.

Previous discussion has suggested that refractory wire-superalloy composites have potential for operation at 1150° to 1200° C (2100° to 2200° F). It may be possible to use convection cooled blades at this higher operating temperature and thereby gain the benefit of the simpler blade design and fabrication while maintaining an equal or lower cooling flow.

Refractory wire-superalloy composites have demonstrated sufficiently high rupture strength and impact values to suggest that they have considerable potential for application to turbine blades at increased operating temperatures. Successful development and application of such composites to turbine blades could permit blade use temperatures as high as 1150° C (2100° F) without the use of diffusion barrier coated fibers, and as high as 1250° C (2300° F) with diffusion barriers. Turbine blade material temperatures of 1150° to 1200° C for a relatively simple convection cooled composite blade might permit gas turbine operation at turbine inlet temperatures over 1650° C (3000° F).

Turbine blade weight for a solid blade of tungsten wire-superalloy composite need not exceed that for conventional superalloys if reasonable measures are taken with the composite. Two variables can be used to overcome the high density of the refractory fiber. The fiber content can be varied along the blade span so as to tailor strength to that needed, and the blade thickness can be slightly reduced near the base as permitted by the improved strength/density properties of the composite.

STRUCTURAL ASPECTS OF COMPOSITES

The first part of this paper has dealt with the material technology aspects of resin and metal matrix composites research at NASA-Lewis Research Center. However, in addition to the material technology, the user or designer must have suitable analysis and design methods available to obtain optimum component or structural designs.

Fiber composite materials require unique analysis methods to determine internal stresses and strains arising from various loading conditions. Because of the nature of the material, conventional stress analysis techniques normally used on homogeneous materials cannot be applied to fiber composite materials. Components made from fiber composites are usually built up using many layers of unidirectional plies. The individual plies can be oriented at any angle to the structural axes. This feature, in effect, permits designing the material for a given application at the same time the component is being designed for structural considerations. Thus, a wide variety of possible internal material configurations and properties are available.

In addition to varying the individual ply orientation angles, the ply stacking sequence and the number

of plies, the fiber content can also be varied from ply to ply. This would normally be done over only narrow limits since the designer usually requires the greatest strength or stiffness with the least weight. However it might be advantageous to vary the fiber content from ply to ply for reasons such as the need to minimize internal stresses resulting from the fabrication process used to make the composite.

Another interesting feature recently being considered is the use of hybrid composites. These are made by using more than one type of fiber within a given laminate or component. Thus, one might include high-strength, low-modulus fibers such as glass or PRD-49 for toughness and impact resistance and at the same time use high strength, high modulus fibers such as boron or graphite for stiffness and primary load carrying capability. Only very limited data are available for such systems but preliminary indications are that the use of hybrid composite components may be very desirable, indeed necessary, for certain applications. For instance, the foreign object damage (FOD) problem, which has been a barrier to the use of resin matrix fiber composite fan blades in advanced turbojet engines, might be alleviated by a judicious combination of fibers in an appropriate matrix.

It can be seen therefore that the many new design variables, the many unique material characteristics of such preferentially oriented anisotropic materials, and the many possible failure modes require novel and sophisticated analysis techniques. These will permit the most efficient use of laminated fiber composite materials for advanced structural applications.

Laminate Design

The ensuing deals with the major factors involved in the development of a practical laminated composite design for application to a complex component. One example of a complex component made using fiber composites is a fan or compressor blade such as shown in Fig. 15. Only the airfoil section of the blade is shown in the figure. The goal is to design a blade of minimum weight within the required constraints, and which can withstand applied and induced steady-state and transient loads imposed during engine operation for thousands of hours. The applied loads are those due to centrifugal force, gas pressure bending, dynamic loads such as transient vibrations and local impact from foreign objects, and environmental such as are caused by thermal gradients. The blade configuration is usually determined by aerodynamic and geometrical constraints and only minor changes, if any, are permissible for structural purposes. Within practical limitations the variables available to the designer are the choice of fiber and matrix, ply orientations, fiber content and number of plies.

Some of the constraints within which the designer must operate, in addition to the geometrical configuration, are the material properties including strengths and stiffnesses, bending and torsional resonant frequencies, untwist and tip deflections, and the flutter speed. In the case of resin matrix composites, a wide variety of fibers and matrices are available for fan and early stage compressor blades. In general, within the available resin-matrix composite systems, the strength necessary to carry the usual loads such as centrifugal, gas pressure, and vibratory is readily available. However, as will be discussed later, the impact strength necessary to survive the impact of foreign objects such as ice-balls and birds is a problem.

Figure 16 is a schematic of part of a cross section of a laminated fiber composite. The orientation of the individual unidirectional plies is determined by strength and stiffness considerations. For instance, in the fan or compressor blade application, radial or near-zero degree plies are needed to carry centrifugal and gas bending loads and maximize bending resonant frequencies. The off-angle plies are needed to minimize untwist and to provide adequate torsional stiffness to avoid torsional flutter problems.

An example of a possible blade layup and stacking sequence taken from Ref. 35 is shown in table V. The problem was to design a high-tip-speed compressor blade having a tip speed of 670 m/sec (2200 ft/sec), a tip radius of approximately 0.72 m (28 in.) and a hub-tip ratio of approximately 0.8. A high modulus graphite fiber in a polyimide matrix with 50 volume percent fiber was selected as the material. The blade layup configuration and operating temperatures are shown for five stations along the span.

Note that the blade cross-section has continuous $\pm 30^\circ$ plies at the surface for torsional stiffness. It also has continuous $\pm 15^\circ$ transitional plies which contribute to the torsional stiffness and tend to minimize interlaminar shear stresses due to applied loads and residual stresses introduced during fabrication. The blade also has radial plies at the core to carry most of the centrifugal load. The radial or zero degree plies are, of course, discontinuous to allow for the taper of the blade and the reduced centrifugal stresses in the outer span of the blade.

Figure 17 shows an example of the transverse stresses in one ply of the laminate. The transverse stress is illustrated here because of possible transply cracking resulting from the curing process alone. The linear laminate theory used to determine the stresses is given in Ref. 36. The ply used for illustrative purposes is the $+30^\circ$ surface ply. If the stresses based only on the external load are calculated, the curve marked M is obtained, indicating a maximum stress of about 2800 N/cm^2 (4 ksi) tensile. If the stresses due to the thermal gradient are included, the curve marked M + T is obtained. This would appear to reduce the stress level to a maximum of about 1400 N/cm^2 (2 ksi) tensile. The curve marked R shows the initial stress state resulting from the curing process. This stress results solely from the assumed 150° C (300° F) cool-down temperature differential from the curing condition. It can be seen that this stress is significantly greater than that resulting from either the mechanical or mechanical plus thermal loading conditions. The transverse ply residual stress calculated for this curing condition is about the same magnitude as the transverse ply strength of the material itself. Figure 17 thus illustrates what has been observed during manufacture, namely, that transply cracking can result from the curing process alone. Finally, the curve marked R + M + T gives the total transverse stress in the ply. As expected, the maximum total stress is greater than any of its components and about equal to the transverse strength of the composite.

Residual Stresses

The effects of symmetry and ply layup sequence on residual stresses are illustrated in Fig. 18. In

this case, ply transverse residual stress is plotted as a function of orientation angle between plies for a 55 percent by volume boron fiber/epoxy matrix composite subjected to a 150° C (300° F) temperature reduction from the cure condition. The three laminates illustrated have the same total number of plies and the same number of plies oriented in a given direction. The difference is in the stacking sequence. It can be seen by the lower two curves that there is little difference in the residual stresses if the plies are regularly interspersed, irrespective of whether the laminate is symmetric, $8[4(\pm\theta), 4(\mp\theta)]$, or unsymmetric, $8(\pm\theta)$. However, it can be seen that if the plies are not interspersed, $8[4(+\theta), 4(-\theta)]$, the residual stresses can be much larger. In this case the increase is more than 50 percent.

The full significance of ply residual stresses resulting from the curing condition has not been determined at this time. Reference 35 indicates that ply residual stresses are largely a function of:

1. Elastic properties of the constituent materials
2. Thermal properties of the constituent materials
3. Fiber volume ratio
4. Ply distance from reference plane
5. Ply orientation relative to composite structural axis
6. Difference between ply temperature and cure temperature

Additional factors including possible creep effects and thermal cycling, in some applications, will probably tend to reduce significantly the magnitudes of the residual stresses. In this connection it should also be noted that it is still not evident how seriously the overall composite strength or stiffness is affected by transply cracks.

Strength Criteria

After a composite system has been selected and a component designed, failure criteria are necessary to determine the structural integrity of the component. A method for determining the strength of a composite under a combined state of stress has been developed at the NASA Lewis Research Center (ref. 37). It involves a two-level, linear, semiempirical theory to predict the failure envelope for a unidirectional filamentary composite subjected to a general biaxial stress condition. The uniaxial strengths of a ply are determined using the first level theory and the properties of the constituent materials. The first level theory is based on a modified rule of mixtures relation and includes empirical factors to relate theoretical predictions with experimental results. The second-level theory is used to predict the failure strength of a ply under a combined stress state and is based on a modified distortion energy principle. This theory contains a correlation coefficient to relate theory and experiment including fabrication process factors. A typical plot of combined stress failure envelopes is shown in Fig. 19.

The von Mises distortion energy theory is a well-known yield criterion for homogeneous metals. The criterion is also frequently used to predict failure and is familiar to many as a single ellipse inclined about 45° to the axis for homogeneous, isotropic materials when plotted as in Fig. 19. The curves shown in the figure for a high modulus graphite/epoxy composite are considerably distorted from ellipses, primarily because of the large difference between the transverse tensile and compressive strengths. Note that there is a series of failure envelopes, the outer one being for the case in which there is no shear on the principal material planes. As the applied shear stress increases, the size of the envelope decreases. If a shear stress equal to the shear strength of the composite is applied to the material, it will fail without the application of any normal stresses parallel or perpendicular to the fiber direction. For this case the failure envelope degenerates to a point at the origin. This failure criterion is applied to the stress state at the ply level. In the case of multidirectional laminates, a laminate analysis such as that presented in Ref. 37 is necessary to find the stress state in each ply before the previously mentioned failure criteria can be applied to the individual plies. In addition, the interlaminar shear stresses must also be calculated and compared with the interlaminar shear strength of the composite.

Impact

One of the most serious problems associated with the use of graphite fiber/resin matrix composites for fan blade applications is the relatively low impact resistance of these materials. Figure 20 shows some impact data obtained at the NASA Lewis Research Center (ref. 38) for unidirectional composites made from a wide variety of fibers embedded in an epoxy resin matrix. It can be seen that the miniature Izod impact energy for the graphite/epoxy specimens tested under longitudinal impact varied by a factor of three from the lowest to the highest value. Specimens utilizing the high modulus organic fiber, PRD-49, had a slightly higher impact energy than the best graphite/epoxy tested, while the S-glass/epoxy system had three times higher impact resistance than the best graphite/epoxy. Results for some hybrid composites are also shown in the figure. It is interesting to note that the impact strength for a hybrid can be greater than that for either of its individual systems as shown by the results for the HTS/Thornel 50-S combination. Data now being obtained by NASA under contract using a different epoxy resin tend to confirm the same relative trends for a series of graphite, glass, PRD-49, and boron fibers embedded in an epoxy matrix.

The laboratory Izod and Charpy data described were obtained at relatively low impact speeds compared to the high velocities encountered under impact from foreign objects on fan blades of advanced turbine engines. In the latter case the relative velocities are 300 to 450 m/sec (1000 to 1500 ft/sec). Higher velocity impact studies are presently being conducted with static and simulated-blade dynamic impact tests in the range of 270 to 450 m/sec (900 to 1500 ft/sec). Five cm by 23 cm (2 in. by 9 in.) static specimens and 7.6 cm by 25.4 cm (3 in. by 10 in.) simulated blades are being impacted by ice, gelatin and steel spheres of various diameters at three different velocities.

Stacking sequence, impact location and impact angle will be varied. Titanium specimens will also be tested for reference and comparison purposes. Finally an analysis will be made to evaluate the results.

Impact resistance for a fiber composite results primarily from fiber breakage and fiber pullout. Reference 38 indicates that the impact strength is proportional to the square of the fiber strength and inversely proportional to the modulus of the fiber and the interface shear strength. Since interlaminar shear strength is a measure of interface shear strength, the impact strength is inversely proportional to the interlaminar shear strength also.

Reference 39 presents a method for determining the stress waves induced in anisotropic plates by transverse, short-duration impact forces. The analysis presented is related to the problem of the impact of small objects such as gravel, ice balls, and small nuts, bolts, and rivets on laminated fiber composite blades. The anisotropy is related to the fiber properties and the layup angles of the individual plies. The magnitudes of the wave velocities in different directions are calculated for graphite/epoxy plates as well as boron/aluminum and glass/epoxy for various layup configurations. The shapes of the wave fronts due to point impact are also presented.

Theoretical as well as experimental work is continuing to relate the design of a fiber composite blade to the foreign object damage problem in advanced turbine engines for aircraft. Composite properties, layup configuration, leading edge protection scheme, and characteristics of the impacting objects are being considered.

CONCLUDING REMARKS

Fiber composite research at the NASA Lewis Research Center directed toward the application of composites to aeronautical and space vehicle systems indicates the following: Significant improvements in the elevated temperature property retention characteristics of high temperature resin/fiber composites can be achieved by modifying the polymer molecular structure, by developing new processing techniques, or by using a combination of both approaches. Considerable success was attained using the combined approach. Polyimide/graphite fiber composites were developed that did not exhibit any loss of 315° C (600° F) flexural and interlaminar shear strengths after 600 hours of exposure at 315° C (600° F). It appears quite probable that resin/fiber composites that can withstand exposure at 315° C (600° F) for several thousand hours and at 370° C (700° F) for a few hundred hours can be developed.

Carbon monofilament with attractive strength values has been produced and is being used in fabrication studies to reinforce aluminum for applications to 482° C (900° F).

Refractory wire-superalloy composites have demonstrated sufficiently high strength and impact values to suggest that these composites have potential for application to turbine blades operating at temperatures to 1200° C (2200° F) and above. Turbine blade weight for a solid blade of tungsten wire-superalloy need not exceed that for conventional superalloys if selective fiber reinforcement is used along the span and if the blade taper is slightly reduced near the base.

Structural analysis methods are available for designing and analyzing structural components made from fiber composite materials. A finite element method was combined with laminate analysis techniques to determine internal loads and stresses. Residual stresses resulting from the curing process were included. A failure criteria based on a semiempirical theory can be used to predict failure at the ply level. These results can be used for modifying and optimizing the laminate configuration. The problem of impact in composites was considered. Izod and Charpy data indicate that S-glass/epoxy has about three times the impact strength of PRD-49/epoxy or the best graphite/epoxy. Theoretical and experimental programs to improve the impact resistance of fiber composite blades are underway.

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TABLE I. - CHARACTERISTICS OF POLYIMIDE RESINS

	Condensation type	Addition type	
		Prepolymer	Monomer
Solvent requirements	High boiling polar solvent, toxic	High boiling, polar solvent, toxic	Low boiling alcohols nontoxic
Solubility, (Solids Content. %)	20 - 40	20 - 40	60 - 70
Viscosity	Medium to High	Medium	Low
Solution Stability	Good	Fair to poor	Excellent
Processability	Very poor	Excellent	Excellent

TABLE II. - PROPERTIES OF VARIOUS 1.27- BY 12.4-CENTIMETER (1/2- BY 4⁷/₈-IN.) POLYIMIDE - GRAPHITE-FIBER COMPOSITES MADE FROM MONOMERIC SOLUTIONS

Sample	Monomeric solution composition ^a	Mole ratio of reactants	Interlaminar shear ^b at 24° C (75° F)		Interlaminar shear ^b at 315° C (600° F)		Composite weight loss ^c after 600 hours in air at 315° C (600° F), percent
			N/m ²	psi	N/m ²	psi	
A	III/I/IV	2/2.34/1.34	74.47	10 800	42.75	6200	17.6
B	III/I/IV	2/4.32/3.32	-----	-----	34.30	4975	17.8
C	III/I/II	2/3.09/2.09	105.49	15 300	41.37	6000	9.5
D	III/I/II	2/6.19/5.19	-----	-----	35.44	5140	28.0

^aI, 4, 4'-methylenedianiline; III, monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid; IV, 2, 5-dicarboxymethoxyterephthalic acid; II dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid.

^bAverage of two to four tests.

^cAverage from two composites.

TABLE III. - WEIGHT LOSS PPQ-I and PPQ-II
EXPOSED TO AIR AT 315° C (600° F)

Polymer type	Film thickness ^a		Weight loss (%) after time (hr) at 600° F in air		
	mm	mils			
			25	403	1076
LMW PPQ-I	0.051	2.0	5.7	6.8	15.6
IMN PPQ-II	0.036	1.4	6.1	6.6	8.6
Random	0.030	1.2	6.6	7.3	10.1
Block	0.043	1.7	6.9	7.5	9.5
LMW PPQ-I	0.051	2.0	4.9	6.2	11.0
IMW PPQ-I	0.096	3.8	7.4	8.4	11.9
Random	0.074	2.9	8.5	9.5	14.0
Block	0.079	3.1	6.6	7.7	11.8

^aFilms were prepared from solutions which
had been stored at ambient conditions for
90 days.

TABLE IV. - EXAMPLES OF BLADE DENSITY CALCULATED BY USING SELECTIVE
REINFORCEMENT WITH STANDARD SOLID BLADE GEOMETRY

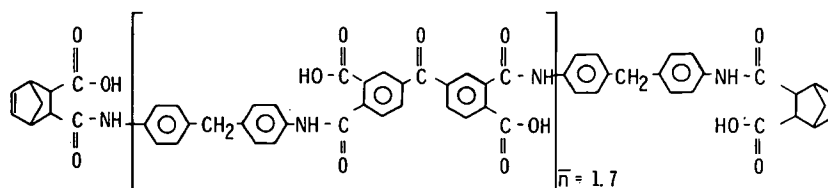
[Calculation based on 1525-m (60 000-in.) stress/density in middle of blade span (critical zone) for 1000-hr rupture failure.]

Composite		Use temperature		Blade density		Maximum wire content, vol. %	Average wire content, vol. %
Matrix	Wire	°C	°F	g/cm ³	lb/in. ³		
Nickel-base superalloy	Uncoated W-Re-Hf-C	1090	2000	9.8	0.35	26	11
		1150	2100	10.2	.37	34	15
IN 100 superalloy	Diffusion- barrier- coated W-Re-Hf-C	1150	2100	8.8	0.32	18	7
		1200	2200	9.4	.34	27	12

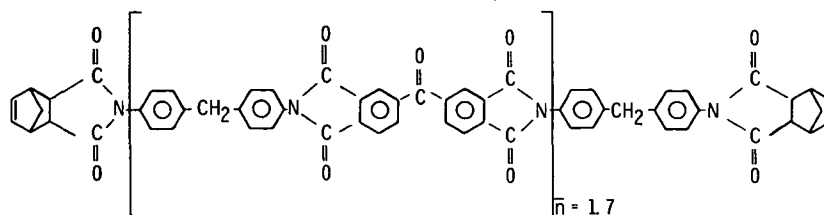
TABLE V. - HIGH-TIP-SPEED COMPOSITE COMPRESSOR BLADE

Thornel-50/Polyimide at 50% FVR; density $\approx 15 \text{ gm/cm}^3$
 (0.054 lb/in.³); tip speed = 670 m/sec (2200 ft/sec);
 tip radius = 72 cm (28 in.); hub/tip ratio = 0.81
 (ref. 35).

Station (percent blade length)	7.9	26.6	50.0	73.1	95.5
Blade temperature (°C)	100	118	148	182	226
Number of plies at maximum thickness	17	16	14	11	8
Surface	4(± 30)	4(± 30)	4(± 30)	4(± 30)	4(± 30)
Transitional	4(± 15)	4(± 15)	4(± 15)	4(± 15)	4(± 15)
Core	9(0)	8(0)	6(0)	3(0)	0(0)



(a) AMIDE-ACID PREPOLYMER



(b) IMIDIZED PREPOLYMER

Figure 1. - P13N prepolymers.

○ P10P AMIDE ACID PREPOLYMER SOLUTION
△ MONOMERIC SOLUTION A

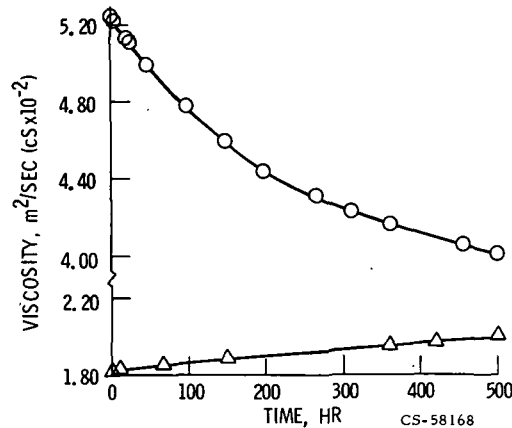


Figure 2. - Viscosity changes of P10P amide-acid and monomeric solution A. Solutions prepared in DMF at room temperature; solids content, 20 weight percent

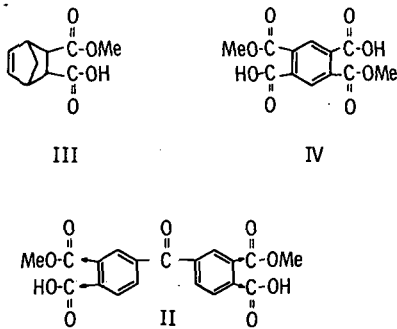


Figure 3. - Structures of modified carboxylic reactants.

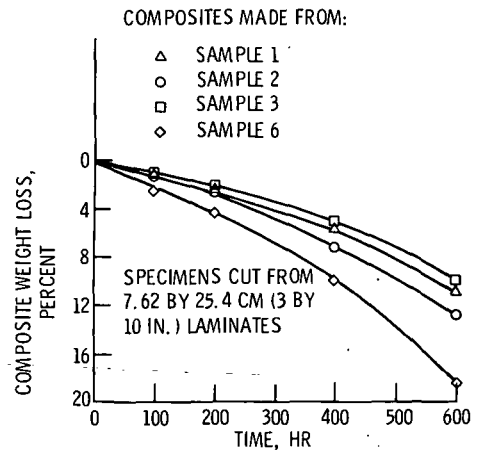


Figure 4. - Percent weight loss of polyimide/HTS graphite fiber composites exposed in air at 315°C (600°F).

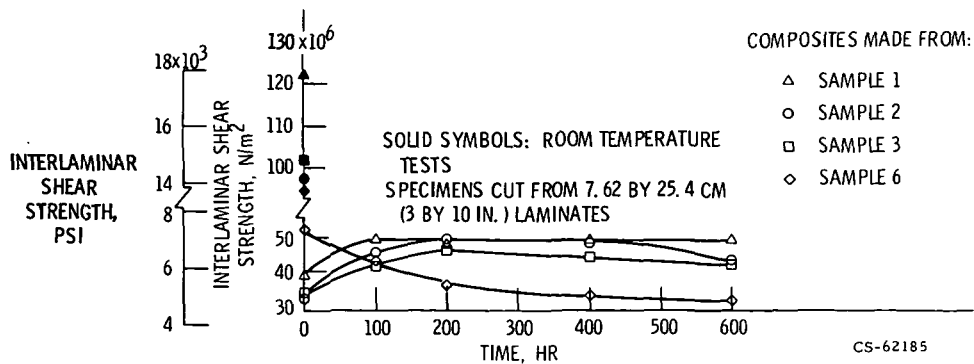


Figure 5. - Interlaminar shear strength of polyimide/HTS graphite fiber composites exposed and tested in air at 315°C (600°F).

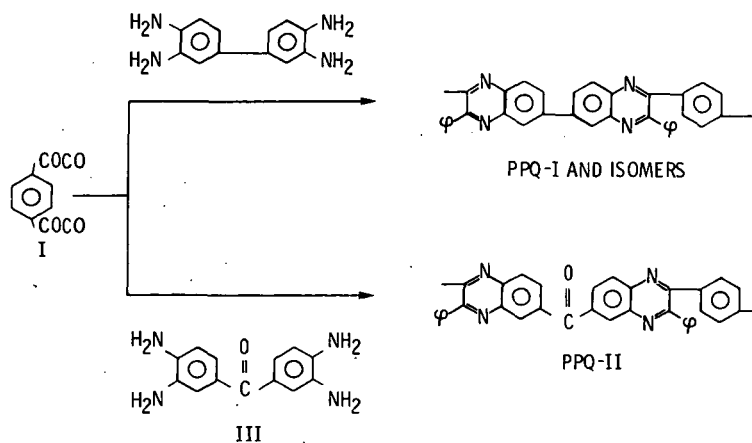


Figure 6. - General synthetic scheme for PPQ-I and PPQ-II.

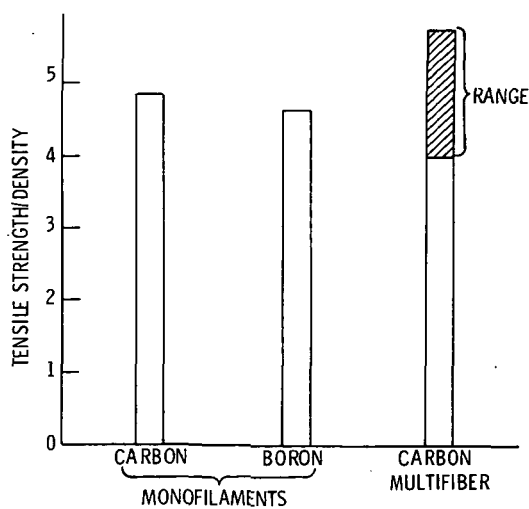


Figure 7. - Relative strength of filaments.

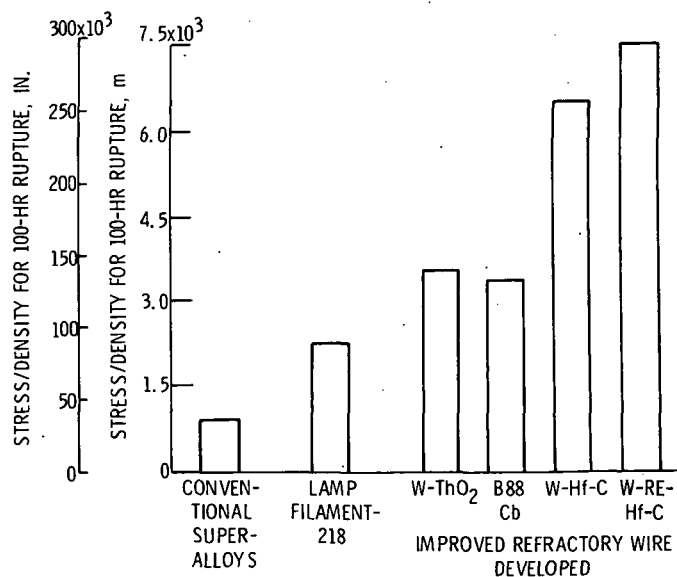


Figure 8. - 100-Hour stress-rupture properties of refractory alloy fiber at 1090° C (2000° F).

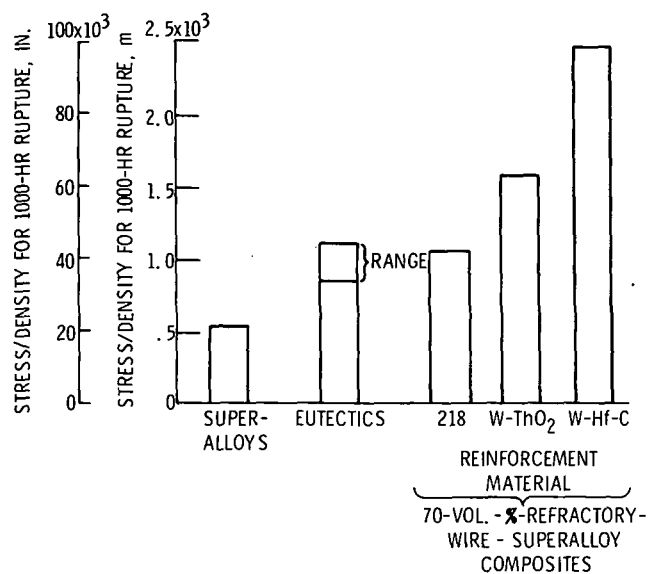


Figure 9. - 1000-Hour stress-rupture properties of refractory-wire - superalloy composites at 1090° C (2000° F).

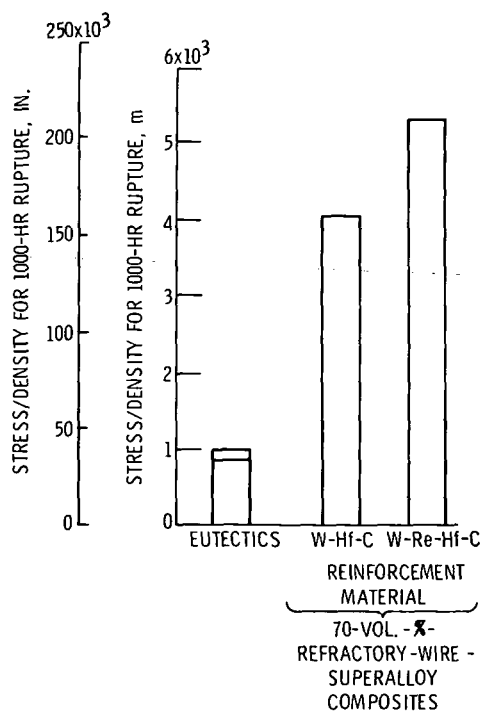
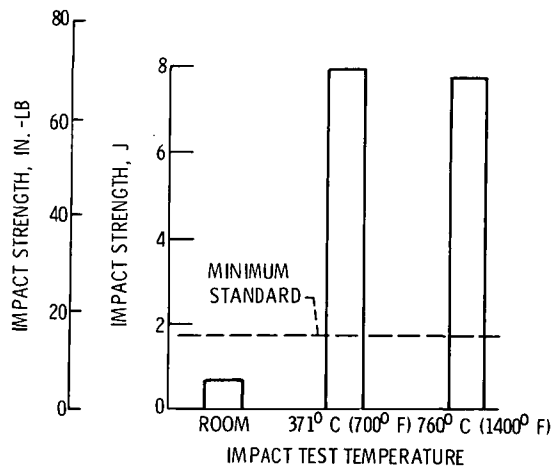
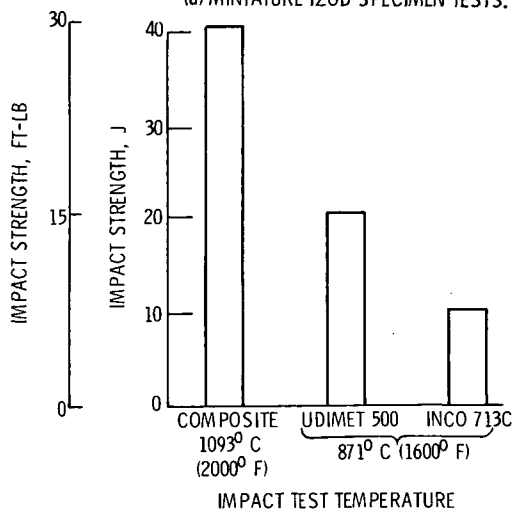


Figure 10. - Projected 1000-hour composite rupture properties with diffusion barriers at 1090° C (2000° F).



(a) MINIATURE IZOD SPECIMEN TESTS.



(b) CHARPY SPECIMEN TESTS.

Figure 11. - Impact strength of tungsten-lamp-filament-wire - superalloy composites for several test temperatures. Composite 60 volume percent wire.

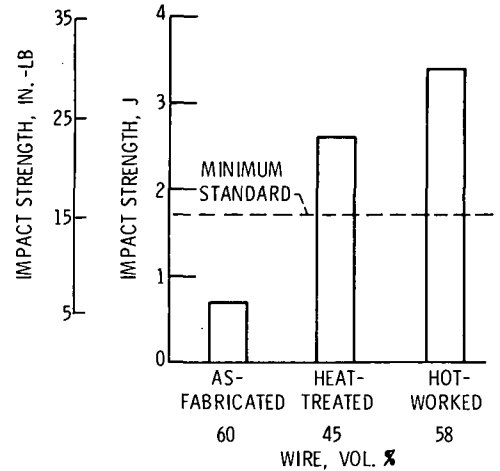


Figure 12. - Improved room-temperature impact strength of tungsten-lamp-filament-wire - superalloy composites. Miniature Izod tests.

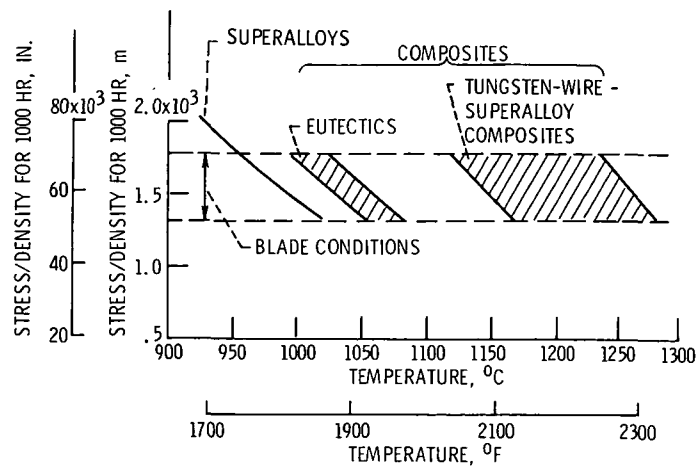


Figure 13. - Potential blade use temperatures for 1000-hour life.

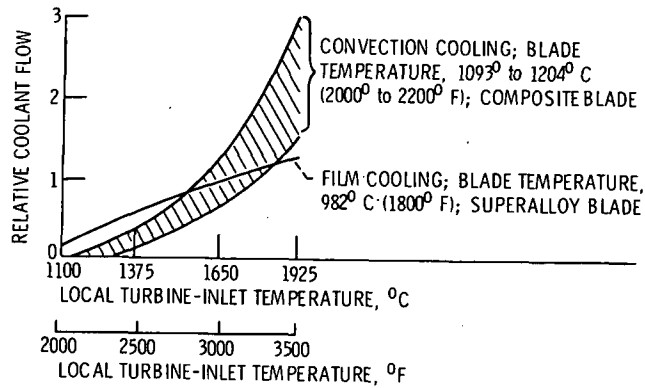
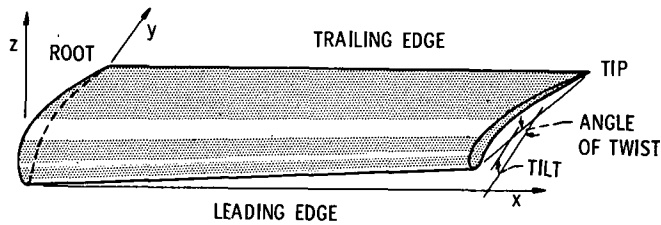


Figure 14. - Effect of blade temperature on cooling airflow requirements.



FIBER COMPOSITE BLADE

LOADS	CONSTRAINTS	DESIGN VARIABLES
CENTRIFUGAL	MATERIAL STRENGTH	FIBER & MATRIX TYPES
GAS PRESSURE	RESONANT FREQ'S	FIBER CONTENT
DYNAMIC	UNTWIST & TIP DEFL'S	NO. OF PLYS
ENVIRONMENTAL	FLUTTER SPEED	PLY ORIENTATIONS

DESIGN GOAL: MINIMUM BLADE WEIGHT

Figure 15. - Definition of turbine blade optimization problem. (Ref. 40.)

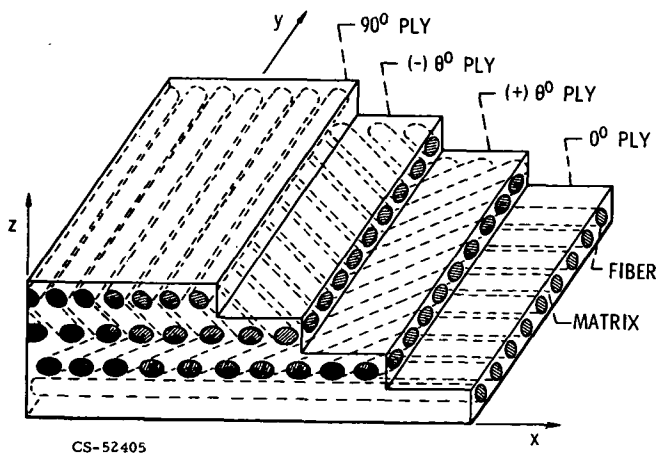


Figure 16. - Typical cross-section of multilayered fiber composite. (Ref. 40.)

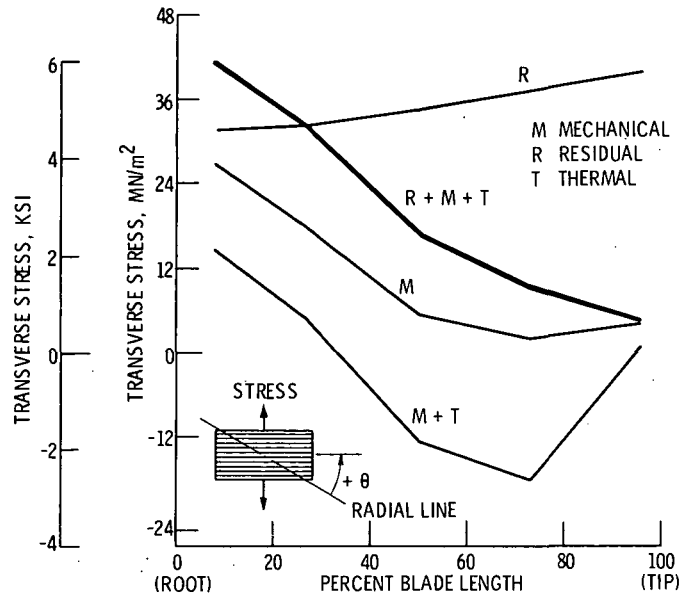


Figure 17. - $+30^\circ$ Surface ply transverse stress of a high-tip-speed composite compressor blade (See table V for composite and loading conditions.) (Ref. 35.)

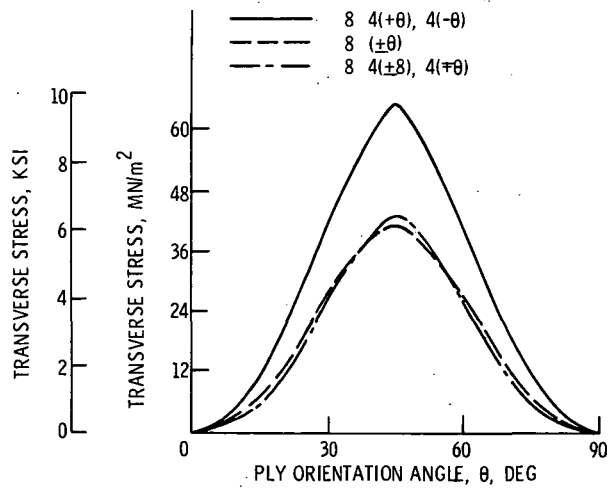


Figure 18. - Ply transverse residual stress in outer ply due to curing for boron/epoxy composites. (Fiber volume ratio = 0.55; $T_{\text{cure}} = 190^\circ \text{C}$ (375°F).) (Ref. 35.)

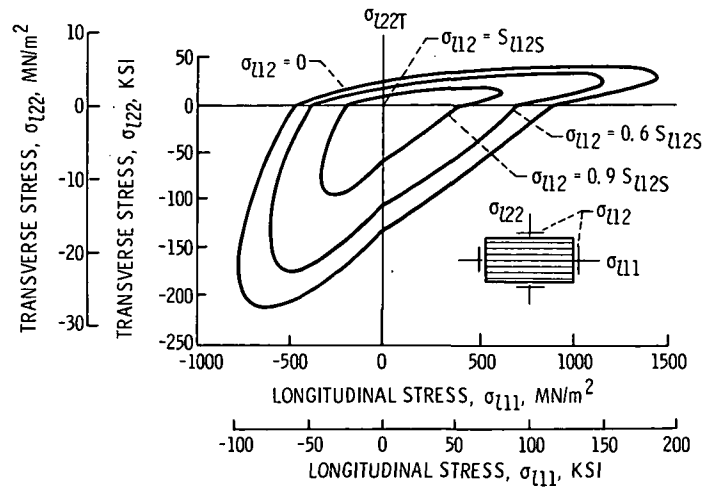


Figure 19. - Combined-stress strength-criterion for Thornel-50 epoxy composite. (Ref. 37.)

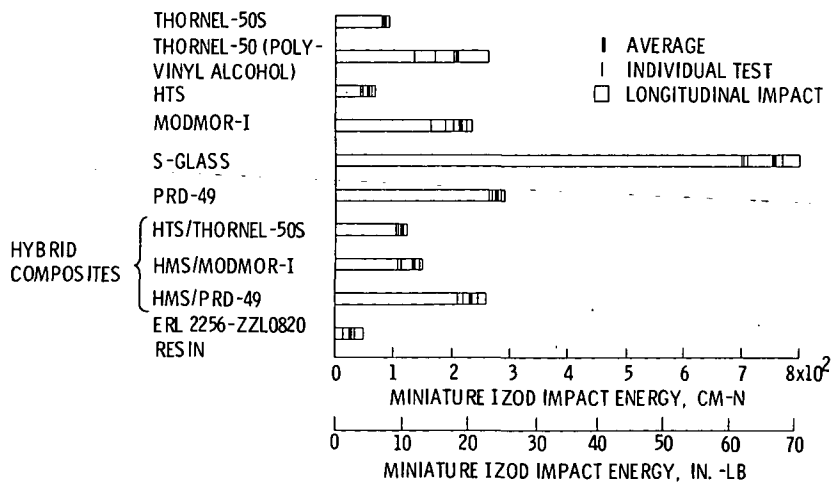


Figure 20. - Miniature Izod impact energy of fiber/ERL 2256-ZZL0820 composites. (Ref. 38.)